

UNIVERSITY OF PENNSYLVANIA

THE ALLOTROPY OF GERMANIUM
DIOXIDE

HORACE R. BLANK

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA

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INTRODUCTION

In previous investigations on germanium and its compounds carried out in this laboratory, Müller noticed that quite frequently when germanium dioxide solutions were evaporated and the residue ignited over a Bunsen or Meker burner, the platinum vessels used for the operation could be cleaned only with the utmost difficulty. The residual GeO_2 did not appear to be completely soluble in boiling water or even in ammonium hydroxide and had to be scraped off the metal. This aroused the suspicion that the oxide might exist in another modification having a much lower solubility than the form ordinarily known.

PRELIMINARY EXPERIMENTS

A large number of preliminary experiments were first carried out in order to determine, if possible, the most favorable conditions under which larger quantities of the insoluble material could be prepared, and to ascertain whether it really was GeO_2 . The formation of insoluble residues had only been observed by Müller on heating GeO_2 which had first been dissolved in water and then evaporated out of the solution. A series of porcelain crucibles containing about 0.5 gram each of germanium dioxide so evaporated were therefore heated to various temperatures between 400° and 1050° C. for periods ranging from two to sixteen hours. On boiling each crucible and its contents with pure water, the greater part of the oxide dissolved, but in every case a small amount of material was left which prolonged boiling for several days with fresh portions of pure water would not take into solution. However, when GeO_2 thus evaporated from water solution was not subjected to any further heating, but was simply boiled with water at once, it proved entirely soluble. The evaporated oxide also dissolved completely in boiling water if it had been melted by heating the crucible in the oxy-gas flame.

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Several attempts were also made to prepare insoluble material by heating the original germanium dioxide directly, without first dissolving it and evaporating the solution, but all of them met with failure. This GeO_2 always proved completely soluble after heating, thus confirming Müller's original observation.

THE INSOLUBLE RESIDUES ARE GeO_2

In order to make certain that the insoluble residues were really germanium dioxide and not any possible impurity which the original material might have contained, a 0.5 gram portion of the evaporated oxide was heated at 830° for sixteen hours. On boiling with water the usual insoluble residue was obtained. This was filtered out, and the filtrate evaporated again into a crucible, and the solid produced by this evaporation was heated to 730° for ten hours. On boiling this with water a second insoluble residue appeared. Repetition of the evaporation and heating on the filtrate from this gave still a third insoluble residue. In no case was the crucible attacked in the slightest by the heated oxide, and if first allowed to stand in cold water over night and then boiled for some hours, the insoluble residues could easily be detached from the porcelain.

A better proof, however, that these insoluble residues actually contained GeO_2 would be to obtain Ge from them. This was done by first repeatedly washing the insoluble material by boiling it several times with fresh portions of pure water, allowing it to settle, and decanting. The well-washed material was then transferred to a platinum dish and the remaining water evaporated off. The residue was then heated until it melted.¹ After melting it dissolved completely in boiling water, and from this solution, after adding pure sulphuric acid to 6N, the white GeS_2 was precipitated by hydrogen sulphide.

Another portion of the insoluble residue, weighing 0.1992 gram, was treated in the same manner, except that it was melted in a silica boat in an electric furnace. The GeS_2 precipitated

¹ This melting is easily observed, as the white solid becomes a transparent glass and can scarcely be seen against the gray platinum. The heat of a Meker burner did not melt the insoluble GeO_2 , and a blast lamp was found necessary.

by H_2S from 6N H_2SO_4 solution was treated several times with nitric acid and ignited over a blast lamp to GeO_2 ; 0.1979 gram of GeO_2 was found, or 99.4 per cent of the original insoluble material. This insoluble substance can therefore hardly be a compound of Ge with some third element, but must be essentially germanium dioxide.

PURIFICATION OF GERMANIUM DIOXIDE

The germanium dioxide used in the preliminary experiments just described was considered pure for all practical purposes, having been freed from arsenic and metals by repeated distillation in hydrochloric acid and chlorine, and precipitation of the sulphide from the distillates by H_2S . These two processes, by which Ge compounds are commonly purified, introduce chlorine and sulphur, respectively, into the product. GeO_2 made by the hydrolysis of GeCl_4 by water contains chlorides, and the oxide prepared by the oxidation of GeS_2 with nitric acid always contains sulphates. It is usually assumed that these impurities will be removed by ordinary ignition, but larger quantities of GeO_2 will always retain readily detectable amounts of each after such treatment.² GeO_2 is therefore readily prepared free from either chlorides or sulphates, but it is not so easily freed from both at the same time.

Sulphates can be removed from germanium dioxide by ignition alone, provided this be continued for a sufficiently long time at a very high temperature. Prolonged ignition over a Meker burner was found insufficient when 10 grams or more of GeO_2 were involved. Immediate fusion of the oxide was also found of no avail, as sulphates could be detected in the water solution of the resulting glass. Ignition at 950°C ., and over, for about thirty-six hours in an electric furnace completely removed the sulphates from 10 to 15 grams of the oxide.

The removal of the last traces of chlorides is more difficult.

² The chlorides can be detected by AgNO_3 in nitric acid solution, and the sulphates by $\text{Ba}(\text{NO}_3)_2$ in the filtrate from the AgCl . Neither of these reagents precipitate pure GeO_2 solutions in the presence of nitric acid.

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Ignition alone, even for thirty-six hours at 950° , was found insufficient on 10 to 15 grams of material. Heating the oxide in a current of superheated steam carried out considerable HCl but proved too slow. Repeated moistening of the oxide with water and heating to 950° was finally found to be effective. It seems probable that the small amount of water which GeO_2 retains at high temperatures³ plays an important part in completing the hydrolysis of GeCl_4 , since unless this water was continually renewed the oxide did not lose all of its chlorides even at 950° .

A portion of the germanium dioxide thus purified completely from chlorides and sulphates also gave an insoluble residue when dissolved, evaporated from solution, and heated to 300° for four hours. While much of the material used in the experiments hereinafter described still contained traces of these non-metallic impurities, sufficient evidence has been obtained to show that the presence of Cl or S is certainly not essential to the formation of the insoluble form of GeO_2 .

VARIATION IN PROPERTIES OF GeO_2 ACCORDING TO METHOD OF PREPARATION

Germanium dioxide, GeO_2 , was first prepared by Winkler,⁴ who described it as a dense white powder, which could apparently be heated to a bright red heat without change. Later investigators, however, found that at high temperatures it melts to "water-like drops."⁵ According to Winkler, GeO_2 is slightly soluble in acids, but readily soluble in alkalis. It dissolves in 247 parts of water at 20° , and in 95.3 parts at 100° , and shows a great tendency to form colloidal solutions. It first gives a suspension with water, which in the cold clears only after some weeks, but which will become clear on heating and will then remain clear on cooling even though supersaturated. The solution shows a distinct acid reaction, and yields on evaporation

³ Dennis, Tressler, and Hance, *Jour. Amer. Chem. Soc.*, **45**, 2033 (1923).

⁴ *Jour. prakt. Chem.*, **34** (N. F.), 211 (1886).

⁵ Abegg's Handbuch, Vol. 4, p. 223.

not germanic acid, but anhydrous GeO_2 . This last observation was confirmed by van Bemmelen,⁶ who unsuccessfully attempted to prepare a definite hydrate by precipitating an alkaline solution of GeO_2 with a current of carbon dioxide.

Winkler also noticed that on evaporation of the solution of germanium dioxide in water, microscopic crystals are formed which are doubly refracting and therefore do not belong to the isometric system. Haushofer⁷ attempted to utilize this behavior in the microchemical detection of germanium, and described the crystals as orthorhombic.

The present investigation has shown that the properties of GeO_2 may vary according to the manner in which it has been prepared. GeO_2 prepared by the hydrolysis of the tetrachloride agreed in properties with that described by Winkler. This germanium dioxide may for convenience be designated in this paper as "hydrolyzed" GeO_2 . As previously mentioned, it always contains small amounts of chlorides. When mixed with water it always gives a milky suspension in the cold. After boiling this mixture for a few minutes it suddenly becomes clear, and the solution can thereafter be kept indefinitely if protected from evaporation. The solution when saturated at boiling temperature, then cooled, and maintained for several days at 25° to 26°C . in presence of an excess of the solid, has been found to contain 0.004684 gram per cubic centimeter.⁸ This GeO_2 dissolves quickly and easily in HF with a hissing noise, as was observed by Krüss and Nilson.⁹ It is attacked by boiling HCl , being volatilized as GeCl_4 .

As far as we have found, the GeO_2 made by the oxidation of GeS_2 with nitric acid has the same properties as has that formed by the hydrolysis of GeCl_4 . Like the "hydrolyzed" GeO_2 , however, it may not always be completely soluble in water after prolonged ignition. (See below.)

All forms of germanium dioxide melt at high temperatures to a viscous liquid, which solidifies to a glass on cooling. This

⁶ *Rec. trav. chim. Pays-Bas*, **6**, 205 (1887), abstr. in *Ber.*, **20**, Ref. 544 (1887).

⁷ *Sitz. Bayer. Akad. Wiss. München*, **17**, 133 (1887), abstr. in *Ber.*, **20**, Ref. 660 (1887).

⁸ Müller and Iszard, *Amer. Jour. Med. Sci.*, **163**, 364 (1922).

⁹ *Ber.*, **20**, 1696 (1887).

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GeO_2 glass when cold is colorless to white. It is fairly hard (scratched by a knife but not by the finger-nail) and very brittle. The unground glass is only very slowly affected by cold water, but dissolves quickly and completely when digested with boiling water. It never, even when finely ground, forms a milky suspension with water before dissolving. GeO_2 kept at or near the melting point in porcelain vessels for some time usually attacks the glaze to a slight extent.

The GeO_2 obtained by the evaporation of a water solution of germanic acid may be called, for the purposes of this paper, "*evaporated*" GeO_2 . When the solution is evaporated slowly, this oxide deposits in a network of minutely crystalline crusts; when the evaporation is rapid it forms a hard, compact mass. The deposit adheres very firmly to the sides and bottom of the vessel in which the evaporation took place. It is very difficult to remove the GeO_2 from glass or porcelain vessels except by practically chiselling it out, but with platinum vessels the dry deposit may be made to crack and peel off from the metal by bending the latter back and forth. The evaporated GeO_2 is only very slowly soluble in cold water, but dissolves completely in boiling water after some hours. On heating it gives small quantities of insoluble GeO_2 at temperatures as low as 200° . Evaporated GeO_2 always retains a small amount of water (up to 2 per cent of its weight) even when in appearance it is perfectly dry.

"*Insoluble*" GeO_2 is obtained by heating "*evaporated*" GeO_2 to any temperature between 200° and its melting point (about 1100°). As explained below, the largest yield is produced in the neighborhood of 380° . After heating, the mass must be boiled thoroughly with a large excess of water, which dissolves the unconverted "*evaporated*" oxide. The insoluble residue may then be recovered by repeated decantation and washing with boiling water. The use of filter paper should be avoided, since GeO_2 is easily reduced by being heated in contact with any kind of organic matter, even with the unconsumed gases of the Bunsen burner.

Insoluble GeO_2 is a white powder, heavy enough to settle very quickly from suspension in water. No exact solubility

measurements were made, but it appears to be quantitatively insoluble in water, even at boiling temperature. In qualitative experiments it did not dissolve in HF, HCl, NaOH, or NH_4OH , even when boiled with these reagents. The behavior with HF is in striking contrast to the "Zischen" and evolution of heat which characterizes the reaction of "hydrolyzed" GeO_2 with this substance. Insoluble GeO_2 appears to melt at about the same temperature as does the hydrolyzed GeO_2 . After melting it solidifies to GeO_2 glass, which dissolves in boiling water as above described. Fusion is therefore the best method of recovering the germanium from GeO_2 which has been converted to the insoluble variety.

Since there was a possibility that the insolubility of this form of germanium dioxide might be due simply to a very slow rate of solubility, we investigated the effect of keeping the insoluble oxide in contact with water for a great length of time. Accordingly 0.0494 gram of the purest insoluble GeO_2 was placed in a flask with about 200 c.c. of pure water, and kept near the boiling point from time to time for one hundred and twenty hours in all. Fresh water was added at intervals to replace that lost by evaporation. No diminution in the amount of insoluble GeO_2 was noticed, and after the experiment 0.0472 gram of it was recovered by filtering the liquid through a Gooch crucible. This would indicate that the "insoluble" GeO_2 is not merely slowly soluble. Its actual solubility in boiling water cannot be greater than 0.00001 gram per cubic centimeter, and may be considerably less.

Under the microscope we were unable to see any distinct crystals in preparations of "hydrolyzed," "insoluble," or "evaporated" GeO_2 . In the case of the last mentioned this is probably because the evaporations have been conducted too rapidly. When examined in polarized light between crossed Nicol prisms, both the hydrolyzed and the insoluble GeO_2 gave a perfectly dark field, indicating that they were isotropic. The evaporated GeO_2 , on the other hand, although no crystals were visible in it, showed numerous illuminated spots between crossed Nicols, indicating that even when evaporated rapidly it is

anisotropic and therefore crystalline, as indeed would be expected from the work of Winkler and of Haushofer.¹⁰

MELTING POINT OF GeO_2

While it has long been known that at higher temperatures germanium dioxide melts to "water-like drops," no attempt has been made, to our knowledge, to determine its melting point until recently, when Nichols,¹¹ while studying the luminescence of GeO_2 at various temperatures, obtained results indicating its melting point as 1400°C . Since preliminary experiments had led us to believe that the melting point was closer to 1100°C ., it seemed necessary to make a more detailed investigation. Accordingly 9.87 grams of carefully purified GeO_2 , freed from traces of chlorides and sulphates as above described, were packed around a Pt-PtRh thermocouple in a transparent silica tube, which was then placed within the tube of an upright platinum-wound, electric resistance furnace. The space between the two tubes was filled with quartz sand to prevent rapid radiation. The top of the furnace was closed with a porcelain lid.

The furnace temperature was now raised until all of the powdered GeO_2 had melted and run down into the lower part of the tube. Four successive cooling curves were then taken, the oxide being remelted and raised to about 1200° to 1300° each time. Readings were taken at fifteen-second intervals, the average temperature interval between readings being about 10° in the neighborhood of 1100°C . The rate of cooling was perfectly regular, and no retardation was noticed at any point. It may, therefore, be concluded that no crystallization takes place when GeO_2 solidifies, even when it is cooled slowly, unless the heat change with 10 grams is too small to be observed in this experiment.

Between 1200° and 1300° molten GeO_2 has about the consistency of molasses, but can easily be stirred with a platinum

¹⁰ *Loc. cit.*

¹¹ *Proc. Nat. Acad. Sci.*, **9**, 248 (1923). In a private communication Dr. Nichols has explained that his material was heated in direct contact with the hydrogen flame, which may have caused some change in its composition.

or silica rod. It regularly becomes less viscous as the temperature is raised. It can easily be drawn out into thin flexible threads, resembling those of glass wool. It shows no tendency to crystallize on cooling, but, like glass, it cracks very easily when large masses are cooled suddenly. Fused GeO_2 does not appear to attack silica chemically at all, but it adheres very firmly to the latter on solidifying, and the difference in their coefficients of expansion almost always results in the destruction of the silica vessel. This great resemblance of fused GeO_2 to glass, and the absence of any thermal effect on cooling, make it seem probable that the solid GeO_2 glass is simply a supercooled, extremely viscous liquid, and does not represent a true solid modification.

In order to determine whether this were the case, the following experiment was performed: A thread of GeO_2 glass was bent into a hook at each end by heating it in the Bunsen burner flame. It was suspended by a platinum wire in the center of an upright electric furnace, closed at the top. From the lower hook hung another wire, to which a weight was fastened so as to hang outside the furnace. The platinum wires were well stretched before using by suspending a heavy weight from them while they were being heated. The thread of GeO_2 used was 41.7 mm. long from suspension to suspension, and had an average diameter of 0.3 mm. The total weight hanging on the thread was 1.26 grams.

The thermocouple was placed beside the thread, and the furnace was gradually heated. The weight first began to move between 725° and 735° . In five minutes it had dropped 0.5 cm., the temperature having reached 740° . The movement then became more rapid, the thread drew out to a fine point, and the weight fell. This behavior is exactly what would be expected if the GeO_2 which has solidified quickly from a state of fusion is a true glass.

The melting point of powdered GeO_2 prepared in various ways was arbitrarily determined by placing a little of the dry powder in a thin silica tube next to the thermocouple in the electric furnace, and noting the temperature below which the particles would not coalesce into tiny globules, as observed under a pocket lens (14 diameters). The purest germanium

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dioxide, which had been ignited to 950° , but which had never been fused, showed globules at 1096° to 1099° . Ground GeO_2 glass, the same material as that used in the experiment described in the preceding paragraph, also coalesced at 1096° to 1099° . This is interesting in comparison with the behavior of the unground glass as above noted. Insoluble GeO_2 gave 1090° to 1091° . It therefore seems that the melting point of any form of GeO_2 , as arbitrarily defined in this paragraph, should be placed between 1090° and 1100° C.

The Pt-PtRh thermocouple and millivoltmeter used in these experiments were calibrated by a determination of the melting points of pure Bi, Pb, Zn, Sb, and Ag metals. The temperatures given are believed to be correct within $\pm 5^{\circ}$ C.

EFFECT OF TEMPERATURE ON YIELD OF INSOLUBLE GeO_2

The preliminary experiments already described indicated that the "insoluble" GeO_2 can be prepared only by heating "evaporated" GeO_2 to various higher temperatures, and that it apparently cannot be easily formed from the ordinary "hydrolyzed" oxide. The amount of insoluble GeO_2 produced seemed to vary quite considerably with the temperature used, and possibly also with the time of heating. The effect of temperature was first investigated, keeping the time constant.

In order to obtain an accurate idea of the amount of insoluble GeO_2 formed in any experiment, it was necessary to devise some means for its quantitative estimation. In the preliminary experiments it was found that it sometimes required boiling with water for about six hours or longer to completely detach all of the GeO_2 from the crucibles used. The complete solution of the evaporated GeO_2 is indicated by the change in appearance of the residue from flaky crusts to a coarse powder, which quickly settles to the bottom of the beaker. We had no means of knowing when all of the unchanged evaporated GeO_2 had been extracted, since in the beginning we had no idea what the solubility of the "insoluble" GeO_2 might be. Neither did we know whether the insoluble oxide might not be changing back into a soluble

variety during the boiling. We therefore adopted the following standard procedure, and all figures relating to yields noted in this paper are given in terms of it:

The porcelain crucible or boat containing the evaporated GeO_2 , after removal from the furnace, was cooled in a desiccator, and was then weighed, placed in approximately 300 c.c. of pure redistilled water, and allowed to stand over night. The mass disintegrated much more quickly when treated in this way than when boiling was begun at once. The mixture was then kept at the boiling point on the hot plate for the next two succeeding days (sixteen hours boiling), the water lost by evaporation being continually replaced. The residue was allowed to settle, and the clear supernatant liquid was decanted while hot through a weighed Gooch crucible. Fresh water was then added to the residue, and the boiling continued for four hours more. The insoluble GeO_2 was then filtered hot through the same crucible, dried at 110° to 120° , and weighed. Drying for two hours at this temperature always gave constant weight.

All of the determinations of the amounts of "insoluble" GeO_2 formed were made in this manner, so that while absolute accuracy in the results is not claimed, they should be directly comparable with one another. Dennis and his associates have shown¹² that GeO_2 retains some water up to 900°C . Upon investigation it was found that the insoluble oxide also retains about 0.5 per cent of its weight of water at very high temperatures, even after drying to constant weight at 110° to 120° . In the figures relating to yields given in the tables below, however, this correction would be inappreciable.

The effect of heating 0.5 gram portions of evaporated GeO_2 at hundred-degree intervals between 200° and 1000° , inclusive, was first investigated. In the first series of experiments each sample of GeO_2 was prepared by evaporating a water solution of the oxide in a weighed porcelain crucible or boat, and we were by no means certain that the conditions of evaporation had been the same in all cases. The first series of results was therefore rather unreliable, but it brought out certain rather striking

¹² Dennis, Tressler and Hance, *loc. cit.*

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facts. When the yield of insoluble GeO_2 , expressed in percentage of the evaporated GeO_2 used, was plotted against the temperature, a fairly symmetrical curve was obtained, which showed a decided maximum.

In the hope that it might be possible to remedy the irregularities shown in this curve by eliminating all possible variation in method of preparation and treatment of the samples, a large volume of GeO_2 solution was evaporated in a platinum dish until a fairly thick crust of evaporated GeO_2 had been obtained. This could be split away from the metal by bending the dish back and forth. The GeO_2 was then powdered and thoroughly mixed, and the entire series of temperature experiments was run on 0.5 gram portions from this same lot (lot No. 1), so that all portions were identical as far as conditions of preparation were concerned. Each sample was weighed into a porcelain boat, and was heated to the desired temperature in a small platinum-wound electric resistance furnace. The temperatures were determined by a thermocouple inserted in the furnace. It was soon found that the evaporated GeO_2 always retained water up to 800° to 900° , as has been shown by Dennis and his associates,¹³ and consequently lost weight during the heating, so that it was necessary to weigh the sample after removing it from the furnace. The average water content (1.73 per cent on lot No. 1) of the samples heated at high temperatures, found in this way, was used to calculate the weight of anhydrous GeO_2 present in the samples heated at low temperatures. Since it was thought probable that slow heating and cooling of the boats might give a different result from a rapid heating and cooling, the procedure finally adopted was to first bring the furnace to the desired temperature, then insert the boat, remove it quickly after the proper time, and allow it to cool quickly in the open to below red heat. It was then placed in a desiccator and weighed when completely cooled.

The results of this series of experiments are shown in Table I. In Fig. 1 the percentage yield of insoluble GeO_2 is plotted against the temperature.

¹³ *Loc. cit.*

TABLE I.—YIELDS OF INSOLUBLE GeO_2 AT VARIOUS TEMPERATURES FOR A CONSTANT TIME OF HEATING

Sample No.	Evaporated GeO_2 used. (Dry weight.) (Grams)	Temperature heated. (°C.)	Insoluble GeO_2 found. (Grams)	Insoluble GeO_2 found. (Per cent of evaporated used.) (Per cent)
0	0.4913	Not heated	None	
1	0.4907	225	0.0004	0.08
2	0.4914	255	0.0027	0.55
3	0.4917	275	0.0091	1.85
4/A	0.4913\	330	f0.0307	6.25
\B	0.4921/		\0.0376	7.64
5	0.4914	350	0.0359	7.51
6	0.4912	380	0.0418	8.54
7	0.4927	430	0.0411	8.34
8	0.4810	530	0.0354	7.36
9	0.4920	630	0.0286	5.81
10	0.4887	730	0.0218	4.46
11	0.4916	840	0.0139	2.83
12/A	0.4913\	940	f0.0131	2.67
\B	0.4915/		\0.0196	3.99
13	0.4908	1040	0.0014	0.29

All samples from the same lot of evaporated GeO_2 (lot No. 1).

All samples heated four hours.

Percentages calculated on the dry weight of the evaporated GeO_2 used.
(See text.)

From these results it will be seen that a slight conversion of the evaporated GeO_2 into insoluble GeO_2 can be noticed at 225° C. The amount converted in a given time increases rapidly with rising temperature to a maximum at about 380°, and then decreases gradually, but some conversion can be observed at any temperature from 225° up to the melting point.

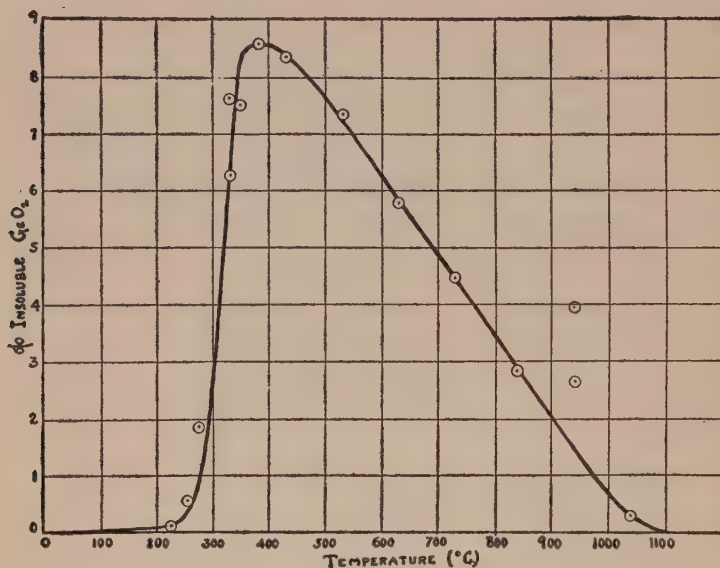


FIG. 1—Yields of Insoluble GeO_2 in Four Hours at Various Temperatures.

POSSIBLE ALLOTROPY OF GERMANIUM DIOXIDE

Since, as has been shown, the insoluble residues formed in all of the preceding experiments appear to consist only of pure GeO_2 , the simplest explanation of the phenomena so far described is that this oxide may exist in two allotropic forms, one of which is soluble in water, and the other insoluble. If this is the case, one form will be stable and the other metastable over any given range of temperature, the pressure being constant (atmospheric). In all cases of metastability, the metastable form always has the higher vapor pressure and the greater solubility. Therefore, at any temperature at which "evaporated" GeO_2 can be converted into "insoluble" GeO_2 , the latter must be the stable form.

The metastable evaporated GeO_2 may have a very slow rate of transformation into the stable insoluble form at the ordinary temperature. When it is heated, however, it is to be expected that the velocity of transformation would be greatly increased.

For "the higher the temperature, and the farther it is removed from the equilibrium point (transition point), the greater is the velocity of change. Above the transition point, these two factors act in the same direction, and the velocity of transformation will therefore go on increasing indefinitely the higher the temperature is raised. Below the transition point, however, the two factors act in opposite directions, and the more the temperature is lowered, the more is the effect of removal from the equilibrium point counteracted. A point will therefore be reached at which the velocity is a maximum. Reduction of the temperature below this point causes a rapid falling off in the velocity of change."¹⁴

The amounts of insoluble GeO_2 produced from the evaporated oxide at different temperatures in the same length of time should be proportional to the velocities of transformation at these temperatures. Then from Fig. 1 we may conclude that the velocity of transformation of the evaporated oxide into the insoluble form increases with rising temperature to a maximum at about 380° , and then decreases gradually from this temperature to the melting point. It would therefore appear that the transition point between the two forms should lie close to, if not above, the melting point, for the transformation in question should not take place at all except at temperatures where the insoluble form is stable. It must not be forgotten, however, that in all of these experiments at high temperatures it was necessary for the evaporated GeO_2 to pass from room temperature through the temperature of maximum velocity of transformation before reaching the temperature of the furnace, and that this fact may possibly have affected the yields of the insoluble oxide at temperatures above 380° .

Determinations Nos. 4A and 4B were carried out at what were supposed to be identical temperatures, and therefore at first sight seem to be very inconsistent. A glance at Fig. 1, however, shows the curve to be very steep at this point, and consequently a very small difference in temperature would make a great difference in the yield of insoluble GeO_2 . When

¹⁴ Findlay, "The Phase Rule and Its Applications," p. 75; Longmans, Green & Co. (1920).

it is remembered that the temperature control was never better than $\pm 5^\circ$ C., and sometimes not quite that good, it is not surprising that concordant results were not obtained here. The same can be said of Determination No. 5 at 350° C. But to Determination No. 12A, at 940° , where the curve should have a much more gradual slope, this explanation would not apply. We therefore repeated this experiment as Determination No. 12B, only to obtain a still higher result. This anomalous result at 940° cannot be explained from the data thus far secured.

The hypothesis of allotropy just presented will also explain the solubility of germanium dioxide glass. If the formation of the insoluble GeO_2 were simply a surface phenomenon due to sintering on heating, fusion of this mass should still further decrease its surface and consequently should lower the solubility still more. *But insoluble GeO_2 can be fused to a glass which is easily soluble in hot water.* The failure to obtain a cooling curve or a definite melting point for the solidified GeO_2 glass indicates that it probably belongs to the same phase as the liquid. If the "equilibrium is chilled" by allowing the molten GeO_2 to cool quickly to room temperature outside the furnace, it is quite probable that this phase of the oxide would remain metastable almost indefinitely. This metastable glass would then be expected to be more soluble than the stable "insoluble" GeO_2 , and as just stated, this is found to be the case.

Although by the hypothesis just given it is possible to explain the formation of insoluble GeO_2 from evaporated GeO_2 , it is not easy to see why any form of this oxide should not yield an insoluble product when heated within the range of temperature shown by Fig. 1. However, repeated attempts to prepare insoluble GeO_2 by heating 0.5 gram portions of "hydrolyzed" GeO_2 directly, without first dissolving it in water and evaporating the solution, resulted in failure. But when larger quantities (10 to 20 grams) of the hydrolyzed oxide, and also of the oxide made by the oxidation of GeS_2 , were ignited to high temperatures in the effort to expel chlorides and sulphates (as described above), insoluble GeO_2 was formed in sufficiently large amounts to be easily identified. It is evidently much more difficult to prepare the insoluble oxide directly from these sources than

from evaporated GeO_2 , but beyond this fact the exact conditions for its direct formation are not yet known.

EFFECT OF TIME OF HEATING ON YIELD OF INSOLUBLE GeO_2

The preliminary experiments had shown that the time of heating, as well as the temperature, was a factor in determining the yield of insoluble GeO_2 which could be obtained from any given quantity of the evaporated material. Before any hypothesis concerning the allotropy of germanium dioxide had been formulated, a series of experiments was undertaken for the study of this effect. Portions of the aqueous solution equivalent to about 0.5 gram of the oxide were evaporated in separate porcelain crucibles, and these were then heated one by one in a gas furnace for periods ranging from fifteen minutes to ten hours, at a temperature of 690° to 720° C. The yields of the insoluble form obtained varied from 4 to over 10 per cent of the original material. When the percentage yields were plotted against the time, some of the results arranged themselves in the form of a rough logarithmic curve.

A curve of this form is what would be expected if the transformation of "evaporated" GeO_2 into "insoluble" GeO_2 were due solely to a change of one allotropic form into another. Such a change must be a monomolecular reaction, and must therefore proceed according to the equation:

$$\frac{dx}{dt} = k(a - x),$$

where "k" is the constant of proportionality, "a" is the amount of the original material, and "x" is the amount changed after time "t." Stated in words, this means that the velocity of such a reaction is proportional to the amount remaining unchanged at any given time. The familiar integrated form of this equation is:

$$t = \frac{1}{k} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{1}{t} \log \frac{a}{a-x}$$

from which

$$\begin{aligned}
 t &= \frac{1}{k} \log \left(1 + \frac{x}{a} + \frac{x^2}{a^2} + \frac{x^3}{a^3} + \dots \right) \\
 &= \frac{1}{k} \left(0 + \log \frac{x}{a} + \log \frac{x^2}{a^2} + \log \frac{x^3}{a^3} + \dots \right) \\
 &= \frac{1}{k} \left(\log \frac{x}{a} + 2 \log \frac{x}{a} + 3 \log \frac{x}{a} + \dots \right) \\
 &= \frac{1}{k} \log \frac{x}{a} (1 + 2 + 3 + \dots) \\
 t &= (\text{a constant}) \log \frac{x}{a}
 \end{aligned}$$

It will thus be seen that if "t" is plotted against " $\frac{x}{a}$ " which in this case is the percentage of insoluble oxide formed, the result should be a logarithmic curve, or if "t" is plotted against the logarithm of " $\frac{a}{a-x}$," as is more usual, a straight line should be produced.

It could therefore be accepted as fairly good evidence that the formation of insoluble GeO_2 really is an allotropic change if such a logarithmic curve and straight line could be obtained.

In order to give this a fair trial experimentally, it is obvious that only the time should be varied, and all other conditions of the experiment should be identical for all of the samples used. In our next experiments identity of the original samples of evaporated GeO_2 was assured by preparing one large lot of the evaporated oxide in a platinum dish in the manner already described, grinding and thoroughly mixing it, and then weighing out exactly 0.5000 gram samples of the resulting powder. Since it was impossible to maintain the temperature of any of our furnaces absolutely constant, identity in the conditions of heating could be approached only by heating all of the samples simultaneously in the same furnace, with as nearly as possible the same exposure to the source of heat.

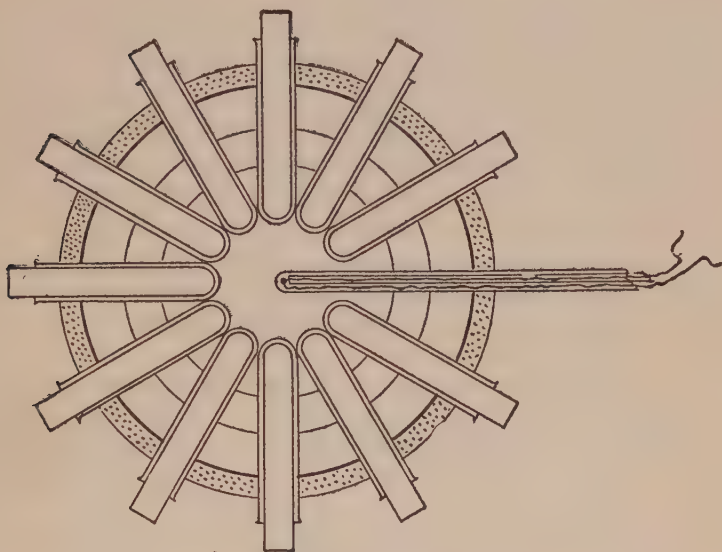


FIG. 2—Diagram of Furnace

For this purpose a special furnace was devised, shown in detail in Fig. 2. The body of the furnace was made of a cylinder of thin sheet iron, within which was placed a small tripod. Around the circumference of the furnace eleven holes were drilled, through each of which a short test-tube made of Pyrex glass was inserted. A twelfth hole carried a smaller tube for the pyrometer (thermocouple). The inner ends of the tubes rested on a ring of asbestos wired to the tripod. The furnace was wrapped with layers of asbestos paper, through which the tubes protruded. The latter were then plastered firmly in place by means of a cement made of shredded asbestos and sodium silicate, which after drying became extremely hard. The entire outside of the furnace was also painted with sodium silicate, which made it quite strong enough to withstand ordinary handling. The top was covered by a cap made by folding up the edges of a circular piece of sheet asbestos. After soaking with sodium silicate, this readily retained its shape. The inside of the furnace was thus made readily accessible by removing the cap and the lid within it. Heat was supplied by a burner playing on the bottom of the furnace. The GeO_2 was placed in small Pyrex

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test-tubes of such a diameter as to slip easily inside the fixed tubes of the furnace. On account of the fear of contamination by plugs of any sort, the ends of the inner tubes were left open.

The furnace was heated to 530° C., and after the temperature had become constant one of the inner tubes containing exactly 0.5000 gram of evaporated GeO_2 was quickly inserted in each of the sockets. At the end of fifteen minutes the first tube was withdrawn, at the end of thirty minutes the second, and so on. The contents of the tubes were shaken out into water, the tubes boiled out, and the insoluble GeO_2 determined by the procedure already described. The results are shown in Table II.

TABLE II.—EFFECT OF TIME OF HEATING WITH TEMPERATURE CONSTANT AT 530° C.

Sample No.	Time heated. (Hours)	Insoluble GeO_2 found. (Grams)	Insoluble GeO_2 found. (Per cent of dry orig.) (Per cent)
1	$\frac{1}{4}$	0.0320	6.51
2	$\frac{1}{2}$	0.0320	6.51
3	$\frac{3}{4}$	0.0323	6.57
4	1	0.0342	6.96
5	$1\frac{1}{2}$	0.0355	7.23
6	2	0.0354	7.21
7	3	0.0354	7.21
8	4	0.0348	7.08
9	6	0.0349	7.10
10	8	0.0351	7.14
11	12	0.0348	7.08
—	—	—	—
0	Not heated	None	

All samples 0.5000 gram. evaporated GeO_2 = 0.4913 gram dry GeO_2 . Percentages calculated on the dry basis.

All samples from the same lot of evaporated GeO_2 .

All samples heated simultaneously in the same furnace.

Highest temperature observed during the twelve hours = 539°. Lowest = 522°.

It is evident that if we allow for the very considerable errors, due to irregularities in temperature, to which this experiment must be subject, we have obtained a practically constant yield of insoluble GeO_2 , regardless of the time of heating. At the time this experiment was made it was thought that the velocity of transformation reached its maximum between 500° and 600° . A careful redetermination of the effect of temperature with the time constant, gave the results already described and shown in Table I and Fig. 1, and placed this point near 380° . The results given in Table I and those in Table II were obtained from the same lot of evaporated GeO_2 (lot No. 1), and the yield for 530° in Table I is nearly the same as the average yield in Table II. The full significance of these results is not yet known, but at least they can have no direct bearing on the question which the constant-temperature, varying-time experiment was designed to answer.

The experiment just described was therefore repeated at a lower temperature, which was more apt to be below the temperature of maximum velocity of transformation, and 280° was selected as the most favorable temperature for this purpose. Lot No. 1 of evaporated GeO_2 having been exhausted, all of the germanium dioxide which was in solution in the filtrates from previous determinations was recovered by precipitation with pure H_2S from sulphuric acid solution. The germanium sulphide obtained was completely oxidized with pure fuming nitric acid, and then, after thorough ignition, was placed in silica boats and melted in the electric furnace. The water solution of this fused oxide was evaporated in platinum dishes to prepare another large lot of evaporated GeO_2 , known as lot No. 2.

The effect of the time of heating at 280° was now determined on eleven samples of lot No. 2, using the same furnace and the same procedure as before. The results are shown in Table III.

It is worthy of note that after being heated at this low temperature every sample became colloidal on first boiling with water, but most of the solutions cleared after prolonged boiling. This was also our experience with the low temperature samples in Table I.

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TABLE III.—EFFECT OF TIME OF HEATING WITH TEMPERATURE
CONSTANT AT 280° C.

Sample No.	Time heated. (Hours.) "t"	Insoluble GeO ₂ found. (Grams.) "x"	Insoluble GeO ₂ found. (Per cent of dry orig.) (Per cent)	$\log \frac{a}{a-x}$	k
1	¼	0.0038	0.76	0.003341	0.01337
2	½	0.0153	3.08	0.013610	0.02722
3	¾	0.0216	4.36	0.019341	0.02575
4	1	0.0277	5.58	0.024963	0.02496
5	1½	0.0313	6.32	0.028315	0.01885
6	2	0.0356	7.18	0.032353	0.01618
7	3	0.0440	8.88	0.040352	0.01345
8	4	0.0500	10.08	0.046157	0.01154
9	6	0.0476	9.61	0.043825	0.00730
10	8	0.0596	12.02	0.055609	0.00695
11	12	0.0656	13.23	0.061623	0.00513
—	—	—	—	—	—
0	Not heated	None			

All samples 0.5000 gram evaporated GeO₂ = 0.4959 gram dry GeO₂. Percentages calculated on the dry basis.

"a" = 0.4959. Values of "x" shown in 3d column.

All samples from the same lot of evaporated GeO₂ and heated simultaneously in the same furnace. Lot No. 2 used. (See text.)

Highest temperature observed during the twelve hours = 284°. Lowest = 272°.

The curve obtained by plotting the percentage yields against the time is shown in Fig. 3. It will be seen that with the single exception of No. 9 all of the results lie close to the expected logarithmic curve. No. 9 refused to clear on boiling, and gave a cloudy filtrate from the insoluble GeO₂, so that it may well be

in error. The plot (not shown) of " $\log \frac{a}{a-x}$ " against "t" from

this same experiment is not a straight line, but another curve, similar in form to that in Fig. 3. How far it deviates from the straight line may be seen by the fact that the value of "k"

(Table III), calculated by dividing " $\log \frac{a}{a-x}$ " by "t," is not

constant.

In the one plot, therefore, we have obtained a curve of the logarithmic form required by our hypothesis, but in the other we fail to get the straight line.

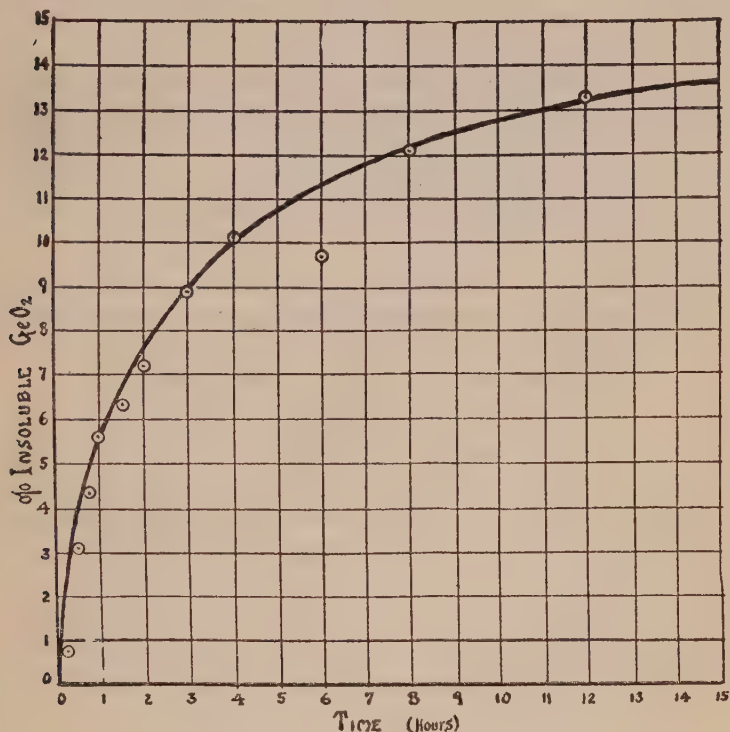


FIG. 3—Yields of Insoluble GeO₂ at 280° C.

POSSIBLE EXISTENCE OF THREE ALLOTROPIC FORMS OF GeO₂

If the change of "evaporated" GeO₂ into "insoluble" GeO₂ is simply a change of one allotropic modification into another,

a monomolecular reaction, its completion should only be a matter of the lapse of a sufficient length of time. This means that the logarithmic curve should be asymptotic to 100 per cent, or that complete conversion should be obtained when "t" equals infinity. The curve shown in Fig. 3 apparently has the logarithmic form, yet if it were prolonged, "t" would equal infinity when the yield was between 14 and 15 per cent. This would indicate that more than about 15 per cent of this lot of evaporated GeO_2 can practically never be converted into the insoluble variety at this temperature, yet the rate at which this conversion proceeds is apparently controlled by the equation of a monomolecular reaction.

If germanium dioxide exists in only two allotropic modifications, only one of which is soluble in water, as already suggested, the evaporated oxide, being completely soluble, must be homogeneous. It is therefore hard to understand why, if sufficient time were allowed, only 15 per cent of it should be convertible into the insoluble form.

As a possible explanation of this behavior we suggest that three different modification of solid GeO_2 may exist, two of which are soluble in a large excess of boiling water. The insoluble form would be the stable one at ordinary temperatures.

Our "evaporated" GeO_2 may then be regarded as a mixture of the two soluble metastable forms, one of which, comprising about 15 per cent of the whole, is converted into the insoluble form much more rapidly than the other, in the range of temperature in which we have experimented. The transformation of this rapidly convertible form reaches its maximum velocity at about 380°C . Since two different preparations of the evaporated oxide did not give the same amount of "insoluble" GeO_2 when heated under similar conditions, it may be supposed that the composition of the mixture varies according to the conditions of the evaporation. While the highest proportion of the easily convertible form in the material used in our experiments would be about 15 per cent, we have not yet conducted any of the evaporations with a view to allowing the greatest possible freedom for crystallization. It seems probable that the ortho-

rhombic crystals described by Haushofer,¹⁵ of the existence of which in our material we have some slight optical evidence, may prove to be the readily convertible form in a pure state. Therefore, if it is possible to prepare large quantities of them we may look for nearly complete conversion of "evaporated" GeO_2 into the insoluble modification.

The supposition that there are three allotropic forms of germanium dioxide is not inconsistent with the fact, previously noted, that it is much more difficult to prepare "insoluble" GeO_2 by heating "hydrolyzed" GeO_2 than by heating the "evaporated" oxide. According to this view the hydrolyzed oxide may be regarded as composed entirely of that metastable form which is the more slowly converted into the insoluble form. The conditions under which this latter conversion reaches its maximum velocity still remain to be investigated.

For the confirmation of the above suggestions much additional knowledge of the behavior of germanium dioxide must be obtained. One salient fact, however, has been repeatedly verified—the "insoluble" GeO_2 becomes easily soluble in water after fusion. As already stated, this seems difficult to explain on any other basis than that of allotropy.

SUMMARY

In addition to the well-known soluble GeO_2 , an insoluble form of this oxide has also been prepared.

The properties of GeO_2 are shown to vary somewhat according to its method of preparation.

Ordinary or "hydrolyzed" GeO_2 , prepared by the hydrolysis of GeCl_4 , has the properties described by Winkler and others.

"Evaporated" GeO_2 is prepared by evaporating a water solution of this oxide (germanic acid). It is anisotropic, and in part, at least, is identical with the crystalline GeO_2 of Haushofer.

"Insoluble" GeO_2 is insoluble in water (about 0.00001 gram per cubic centimeter dissolves at boiling temperature), and appears to be unattacked by HF , HCl , NaOH , and NH_4OH ,

¹⁵ *Loc. cit.*

all of which readily dissolve the ordinary hydrolyzed GeO_2 . It is formed by heating evaporated GeO_2 to any temperature between 225° and 1040° C. The evaporated GeO_2 is not all converted. Under certain conditions, as yet very incompletely studied, insoluble GeO_2 may be formed by heating the hydrolyzed oxide directly. *After fusion to GeO_2 glass this insoluble modification becomes soluble.*

All forms of GeO_2 fuse at about 1100° C. to a viscous liquid, which solidifies to a glass and not to a crystalline modification. Attempts to determine the melting point by means of a cooling curve failed for this reason. Threads of GeO_2 glass can be made to soften at temperatures (740°) far below the melting point. GeO_2 glass, even in lump form, is very readily soluble in hot water.

The melting point of any form of GeO_2 , determined by observing the coalescence of fine particles, appears to lie between 1090° and 1100° C.

Experiments are described which show that the yield of insoluble GeO_2 , formed by heating evaporated GeO_2 at different temperatures for the same interval of time, increases up to 380° C., and then decreases to the melting point. The curve is shown.

Further experiments show that with the temperature constant at 530° , the yield of insoluble GeO_2 formed from evaporated GeO_2 remains practically constant for periods of heating ranging from fifteen minutes to twelve hours. At 280° , however, the yield increases according to the curve for a monomolecular reaction, but the reaction reaches completion when only about 15 per cent of the evaporated GeO_2 has been converted to the insoluble form.

The foregoing facts can be accounted for by supposing that GeO_2 exhibits allotropy, but their explanation on the basis of only two forms of this oxide is shown to be inadequate.

Consequently the possible existence of three forms of GeO_2 is suggested, considering the "insoluble" oxide as the stable form at ordinary temperatures. The "evaporated" GeO_2 may be regarded as a mixture of two metastable forms, one of which is converted to the insoluble form much more rapidly than the other. The experimental results obtained are discussed from this point of view.

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